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N00014-79-C-0668

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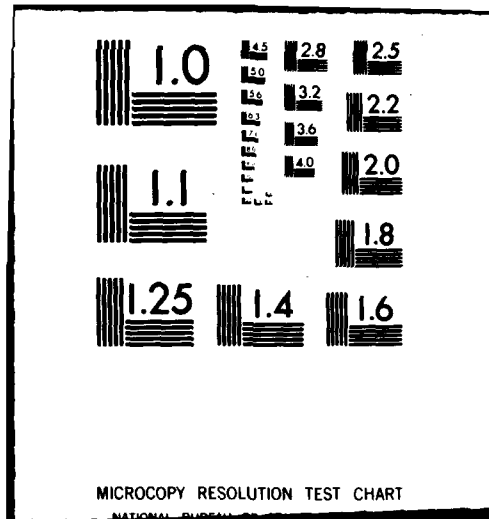
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REPORT DOCUMENTATION PAGE

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BEFORE COMPLETING FORM

1. REPORT NUMBER

Technical Report No. 1

2. GOVT ACCESSION NO.

AD-A093 693

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle)

Motional Correlation Time of Dilute ^{111}Cd
Impurities in Liquid S and Se

5. TYPE OF REPORT & PERIOD COVERED

(9) Interim rept.

6. PERFORMING ORG. REPORT NUMBER

(14) HR-1

8. CONTRACT OR GRANT NUMBER(s)

(15) N00014-79-C-0668

7. AUTHOR(s)

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County)

9. PERFORMING ORGANIZATION NAME AND ADDRESS

Oregon State University
Corvallis, OR 9733110. PROGRAM ELEMENT, PROJECT, TASK
AREA & WORK UNIT NUMBERS

NR-056-721

11. CONTROLLING OFFICE NAME AND ADDRESS

Office of Naval Research/Chemistry Program
Arlington, VA 22217

12. REPORT DATE

(11) 10 December 1980

13. NUMBER OF PAGES

4 (12) 19

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)

15. SECURITY CLASS. (of this report)

Unclassified

15a. DECLASSIFICATION/DOWNGRADING
SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

To be published in Proceedings of the 5th International Conference on
Hyperfine Interactions, Berlin, 1980.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

correlation time

 ^{111}Cd impurities in liquid S and Se

time differential perturbed angular correlation

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The correlation time τ_m of dilute ^{111}Cd impurities in liquid Se and S was measured using the TDPAC technique. For Se, the data are described by an Abragam-Pound attenuation between 443 C and 944 C. The temperature dependence of τ_m shows Arrhenius behavior, with excitation energies of $(0.360 \pm 0.004)\text{eV}$ and $(0.47 \pm 0.06)\text{eV}$ below and above ~ 850 C, respectively. τ_m varies from 18 ps at 944 C to 306 ps at 443 C. At lower temperatures, deviations from Abragam-Pound relaxation are observed. For sulfur, only data above 650 C show single-exponential attenuation, with no clear-cut temperature dependence.

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Impurities in Liquid S and Se

by

D. K. Gaskill, J. A. Gardner, K. S. Krane,

K. Krusch, and R. L. Rasera


Prepared for Publication

in the

Proceedings of the 5th International Conference on
Hyperfine Interactions, Berlin, 1980

Oregon State University
Department of Physics ✓
Corvallis, OR 97331

December 10, 1980

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1

MOTIONAL CORRELATION TIME OF
DILUTE ^{111}Cd IMPURITIES IN LIQUID S AND Se

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The correlation time τ_m of dilute ^{111}Cd impurities in liquid Se and S was measured using the TDPAC technique. For Se, the data are described by an Abragam-Pound attenuation between 443 C and 944 C. The temperature dependence of τ_m shows Arrhenius behavior, with excitation energies of $(0.360 \pm 0.004)\text{eV}$ and $(0.47 \pm 0.06)\text{eV}$ below and above ~ 850 C, respectively. τ_m varies from 18 ps at 944 C to 306 ps at 443 C. At lower temperatures, deviations from Abragam-Pound relaxation are observed. For sulfur, only data above 650 C show single-exponential attenuation, with no clear-cut temperature dependence.

The elements sulfur, selenium and tellurium have been extensively studied in the liquid state on account of their interesting electrical and physical properties.¹ According to current understanding, these materials exist in the liquid in the form of chain- or ring-shaped molecules, depending on the material and temperature range. Their electrical properties are strongly influenced by bonding irregularities in the predominant structure, such as chain ends, branches or impurities. As temperature increases, the relative concentration of these defects in bonding also increases, with a concomitant increase in the conductivity. Physically, the viscosity of the liquids decreases rapidly with increasing temperature, suggesting that the liquids undergo marked structural changes (ring-chain transformation, and shortening of chain length with increasing temperature, for example). Although powerful tools such as NMR, neutron scattering, and viscosity measurements, among many others, have been used to study these materials, a complete understanding of the dynamical behavior of these liquids is still lacking.

We describe here an application of time-differential perturbed angular correlation (TDPAC) to the study of molecular dynamics in liquid S and Se. The probe chosen was ^{111}In , which decays via a 171-247-keV cascade to ^{111}Cd . Aside from its well-known favorable properties for TDPAC measurements, this probe has other characteristics which make it suitable for use here. Indium, the parent species, dissolves readily in Se and S if the concentration is kept sufficiently low. Further, the daughter Cd ions have a high affinity for the chalcogens, as evidenced by the available phase information on these two systems. Furthermore, the 0.2-nsec lifetime of the initial state of the gamma cascade used is greater than the correlation times of the liquid over the temperature range measured, thus allowing sufficient time for the probe to bind to the host molecule before the cascade begins.

A previous TDPAC study of the dynamics of liquid Se using ^{111}In was made by Rasera and Gardner,² who found that, in the temperature range between 490 C and 900 C, the observed attenuation could be described using the classic Abragam-Pound³ limit of fast quadrupolar relaxation with a relatively weak average quadrupole interaction strength. However, the samples used in ref. 2 were made by direct alloying of electroplated indium containing the parent activity, with selenium. With this

*Supported by ONR Grant N00014-79-C-0668.

technique the minimum dilution achievable was approximately 0.05 at.% In; furthermore, variations in the concentration of indium caused precipitation of In_2Se_3 at low temperatures in some samples. The experiments described in this paper make use of a different sample-making technique in which the carrier-free radioactivity is dissolved directly in the host material. The samples thus produced are much more dilute, allowing extension to lower temperatures without precipitation of the sesquichalcogenide. Each sample was sealed in quartz under vacuum, and placed in a temperature-controlled vacuum furnace for measurement. The TDPAC spectrometer used is a four-detector, four-channel array using NaI(Tl) detectors.

The measurements on selenium over the temperature range from 443 C to 944 C show a behavior consistent with that previously found in ref. 2. The data were fit to the Abragam-Pound time-dependent attenuation factor

$$G_2 = e^{-\lambda_2 t}$$

where for quadrupolar relaxation with intermediate-state spin 5/2, $\lambda_2 = 2.49 \tau_m \langle \nu_Q \rangle^2$. If the average quadrupole interaction strength $\langle \nu_Q \rangle$ is taken to be independent of temperature, λ_2 is proportional to the correlation time τ_m , independent of the value of $\langle \nu_Q \rangle$. Figure 1 shows the logarithm of the measured values of λ_2 plotted against reciprocal temperature. In the temperature range between 440 C and 850 C, the data fall on a straight line, indicating that the correlation time follows an Arrhenius law, i.e., $\tau_m = \exp(E_m/kT)$. This dependence on temperature is characteristic of a thermal activation process. In this region, the slope of the line yields an excitation energy $E_m = (0.360 \pm 0.004)\text{eV}$. At temperatures above approximately 850 C, the data follow a somewhat steeper slope; the dotted line in Fig. 1 corresponds to $E_m = (0.47 \pm 0.06)\text{eV}$. It is not clear whether the temperature dependence in this region is in fact linear, due to the short temperature range. On account of the high internal pressures in the quartz sample containers, higher temperatures than 950 C were not attempted. At the other end of the temperature range we found that for temperatures between 440 C and the melting point of Se, the measurements showed deviations from the single-exponential Abragam-Pound attenuation. The nature of this deviation, which is characterized by an oscillatory component to the attenuation, is different from that observed in ref. 2 due to precipitation of In-Se compounds, and may possibly be due to the departure of the system from the realm of validity of the Abragam-Pound assumptions.

In order to extract a correlation time from the measurements one must know the average interaction strength $\langle \nu_Q \rangle$. In the absence of direct measurement, this quantity must be estimated. In ref. 2 this quantity was estimated to be 125 MHz, with an uncertainty of a factor of two. Using this estimate, we find that the measured correlation time τ_m ranges from 18 ps at 944 C to 305 ps at 443 C. Given the uncertainty in $\langle \nu_Q \rangle$, it is possible that the correlation times at lower temperature slow to the point where a more general relaxation model than that of Abragam-Pound must be applied.

The experiments on liquid sulfur in the same temperature range yielded considerably less clear-cut results. Above 650 C, the measured attenuation factor G_2 is exponential in form, as in selenium. Following the argumentation of ref. 2 concerning the average field gradient, we obtain correlation times in this temperature region which are longer by a factor of 2-3 than in Se. However, there is no unambiguous linear relationship between $\ln \lambda_2$ and $1/T$; thus it appears open to question whether these correlation times are caused by a thermal activation process.

Below 650 C the data were not reproducible in different samples. The difficulties may perhaps be traced to the differing phase properties of the In-S system. Also, the conductivity of liquid sulfur in the temperature range investigated here is considerably less than that of Se at corresponding temperatures. Thus, after-effects of the electron-capture decay of ^{111}In may be important in the lower temperature regions, where S is a rather good insulator. It is in these regions

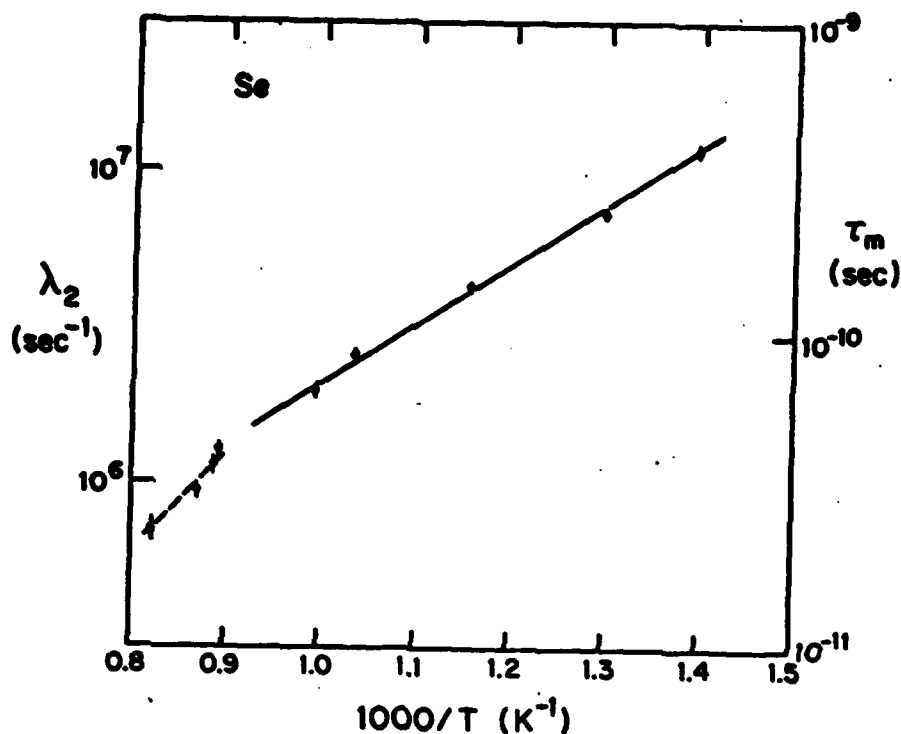


Figure 1. Time-dependent attenuation parameter λ_2 plotted against reciprocal temperature for ¹¹¹Cd in Se. The right-hand scale gives the corresponding correlation time using an assumed $\langle \nu_Q \rangle$ of 125 MHz, as discussed in the text.

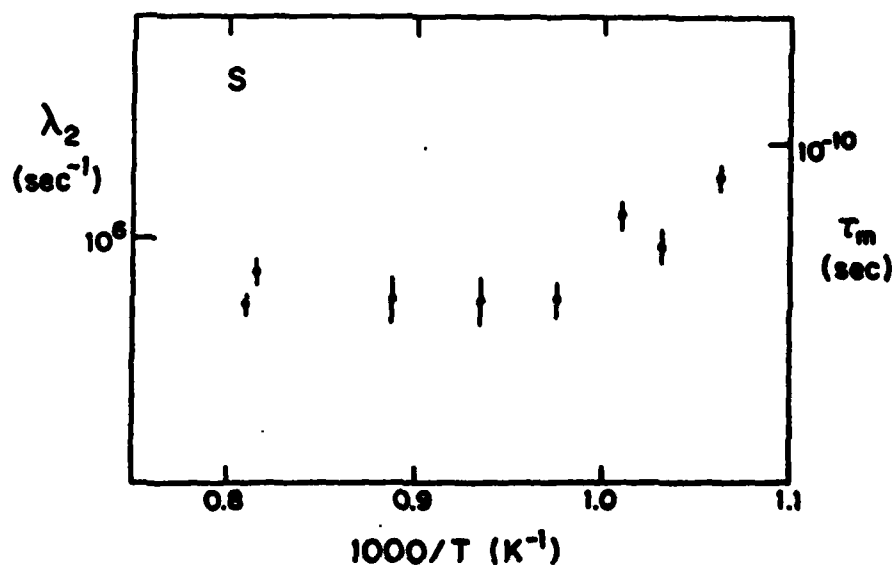


Figure 2. λ_2 plotted against reciprocal temperature for ¹¹¹Cd in S. For the correlation time scale, a value for $\langle \nu_Q \rangle$ of 80 MHz extracted from the static interaction in a solid sample at room temperature was used.

where difficulties were encountered with reproducibility among samples; differing impurity levels can have a marked effect on the concentration of available electrons.

There are several different possibilities for the physical mechanism giving rise to the observed correlation time in the selenium measurements. If, as is indicated by the high melting points of Cd-Se compounds relative to that of Se, the Cd-Se bond is stronger than the Se-Se bond, then the observed correlation time is due to the dynamical behavior of the Se-molecule -- either bond-breaking between Se atoms, or tumbling of the molecule. While it is probable that both these mechanisms -- and possibly others, such as Cd-Se bond breaking -- are present, we have no independent means for distinguishing the dominant process. What we can say, however, is that the measured correlation time is characteristic of the dominant mechanism, and so represents a lower limit for the bond lifetimes.

The values obtained for E_m and τ_m in selenium can be compared with the very few measurements of similar quantities obtained with other experimental techniques. The viscosity as a function of temperature is related to these quantities, but the quantitative relationship is not well understood. Nevertheless, Rialland and Perron⁴ obtained a value of 0.50 eV for the viscosity activation energy between 500 C and 900 C. Acoustic attenuation measurements⁵ yield a rough value for τ at 400 C of 5 ns, which is somewhat longer than an extrapolation of the current experimental results to this temperature. Finally, neutron scattering experiments⁶ have found a diffusion time of 1.5×10^{-11} s at 450 C, much shorter than can be immediately understood. This last effect has also been seen in other molecular liquids, and is not well understood. In each of these techniques, the various dynamical mechanisms play roles of differing importance; more experimental data on similar systems over the same range of temperature may allow a more detailed interpretation of the measured quantities in each case.

ACKNOWLEDGMENTS:

This work was supported in part by the Office of Naval Research.

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